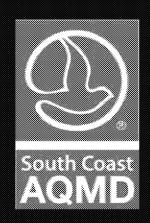
Status Update on PR 1410 – Hydrogen Fluoride Storage and Use at Petroleum Refineries



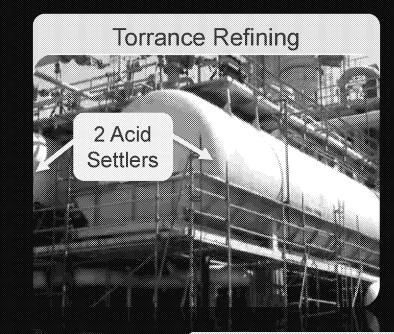
Governing Board Meeting

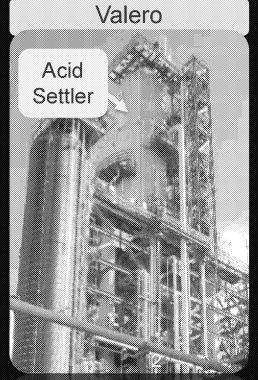
February 1, 2019 Diamond Bar, California

HF Background

- Hydrogen fluoride (HF) is a strong, potentially lethal acid
- HF is used to produce alkylate which is a blending component of high-octane gasoline
- Used at two California refineries: Torrance Refining and Valero
- Both refineries use modified HF (MHF), designed to reduce its exposure

Approximate Volumes (gallons)				
	Valero (Wilmington)	Torrance Refining		
Storage on-site	55,000	25,000		
Use in acid settlers	7,000 with baffle	12,000 in two tanks		





Regulatory Background

- April 1991 Board adopted Rule 1410 –
 Hydrogen Fluoride Storage and Use
 - □ Established a 7-year phase-out of HF unless a performance standard could be achieved
 - □ Required interim control measures
- Lawsuit challenged Rule 1410
 - □SCAQMD's authority to phase out HF was upheld¹
 - "[T]he Legislature clearly intended to vest AQMD with the authority to adopt preemptive measures designed to prevent air pollution episodes"
 - □Rule invalidated due to procedural error in circulating CEQA document

(Adopted April 5, 1991)

RULE 1418. HYDROGEN FLUORIDE STORAGE AND USE

(a) Puspos

This rule is intended to minimize the possibility of larm to the public due to an accidental release of hydrogen fluoride.

(b) Applicability

All subsections of this rule apply to refrigerant production facilities and peroleum refineries. Any other facility which stores or uses hydrogen fluoride must comply with subvarantaphs (304)(A) and (6×5) only.

(c) Definition

- ALKYLATION is a process in which high-actane components for gasoline are obtained from the combination of an isoparaffin and olefins in the presence of a catalyst.
- (2) ATMOSPHERIC HYDROGEN FLUORIDE DETECTION AND ALARM SYSTEM is any continuous sensor specific to hydrogen fluoride that activates a local or remote audible slarm systems(s) when the concentration of hydrogen fluoride exceeds six parts per million in the ambient six
- (3) CONTAINMENT SYSTEM is any system that is designed to collect or hold, and to neutralize or user all hydrogen financies and water that is required to comply with subparagraph (dy.2080(iii), containing-ranoff meserial from hydrogen fluoride leading, unloading, transfer, storage and processing equipment areas.
- EMERGENCY ISOLATION VALVE is any valve activated by remote council to shot off the flow of materials containing hydrogen fluoride.
- (5) EVACUATION SYSTEM is any process capable of emptying substantially zell hydrogen fluoride from process, storage and transfer equipment, including, but not limited to, sanks, pamps, papes, and processing equipment.
- (6) FACILITY is any collection of equipment that stores, processes, loads, unloads or transfers hydrogen fluoriste, which are located on one or more configuous properties in actual physical contact or separated solely by a public roadway or other public right-of-way, and are owned or operated by the same person for by personal under common control).

1438 - 1

Decision Not to Pursue Re-Adoption of Rule 1410

1991

Mobil Refinery² entered into a court consent decree

- ☐ Phase-out of HF by 1997 or
- □ Allow use of MHF if demonstrates no formation of dense vapor cloud

1999

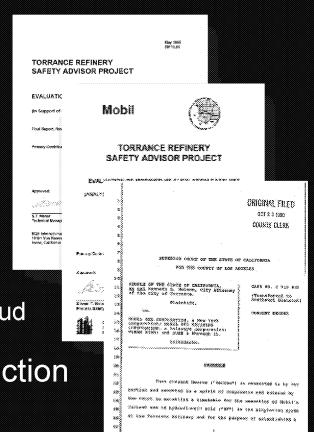
Consent decree was changed to allow a significant reduction of the modifier

2003

SCAQMD signed MOU with Ultramar³ to phase-out HF and allow use of MHF

2017

Torrance Refining provided SCAQMD with confidential information about MHF



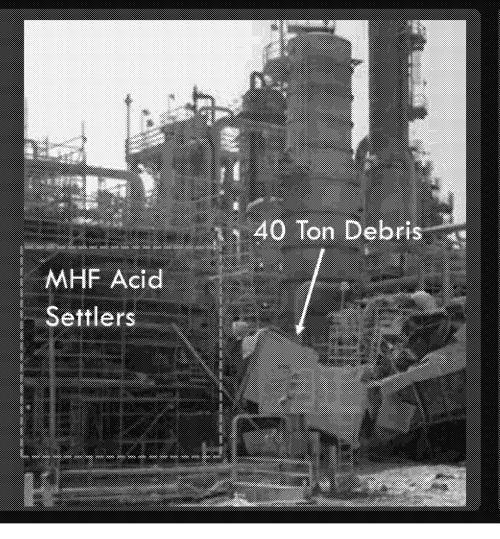
² Currently Torrance Refining Company

³ Ultramar is currently Valero

Events Leading to the Investigative Hearing in April 2017

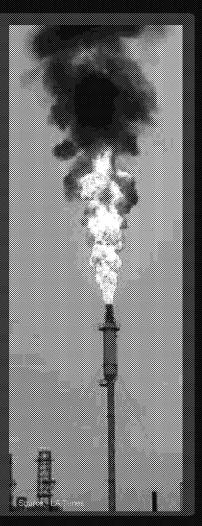
2015

"Near Miss"
40 ton
debris lands
within 5 feet
from MHF
tanks at
Torrance
Refining



2016-2017

Series of large flaring events and fire event that raised concerns about safety at Torrance Refining



10 MHF Leaks Since 2017

April 4, 2017 Torrance 1.4 PPM Nov. 13, 2017 Valero 7 PPM Dec. 22, 2017 Torrance 10 PPM⁴ June 16, 2018 Valero 10 PPM⁴ Jan. 19, 2019 Torrance 7.2 PPM

1 2 3 4 5 6 7 8 9 10

Sept. 6, 2017 Valero 10 PPM⁴ Nov. 27, 2017 Valero 10 PPM⁴ June 2, 2018 Valero 9 PPM Dec. 22, 2018 Torrance Unknown⁵ Jan. 25, 2019 Torrance 10.45 PPM

⁴ HF point sensors can only measure up to 10 ppm. Concentrations could have been higher.

⁵ 5 gallons of HF released at loading rack. No HF point sensors at loading rack. Closest HF point sensor is ~ 25 feet.

Public Process Following Investigative Hearing

1,300+ Comment Letters and Emails

- 500+ commenters opposing a phase-out
- 800+ commenters supporting a phase-out
- 7 letters from elected officials

Multiple Site Visits

 Observed current mitigation and safety measures at both refineries

19 Individual Stakeholder Meetings

- 12 meetings with refineries
- 5 meetings with community groups
- 2 meetings with EPA/Cal OSHA

Comment Letters and Emails

Site Visits

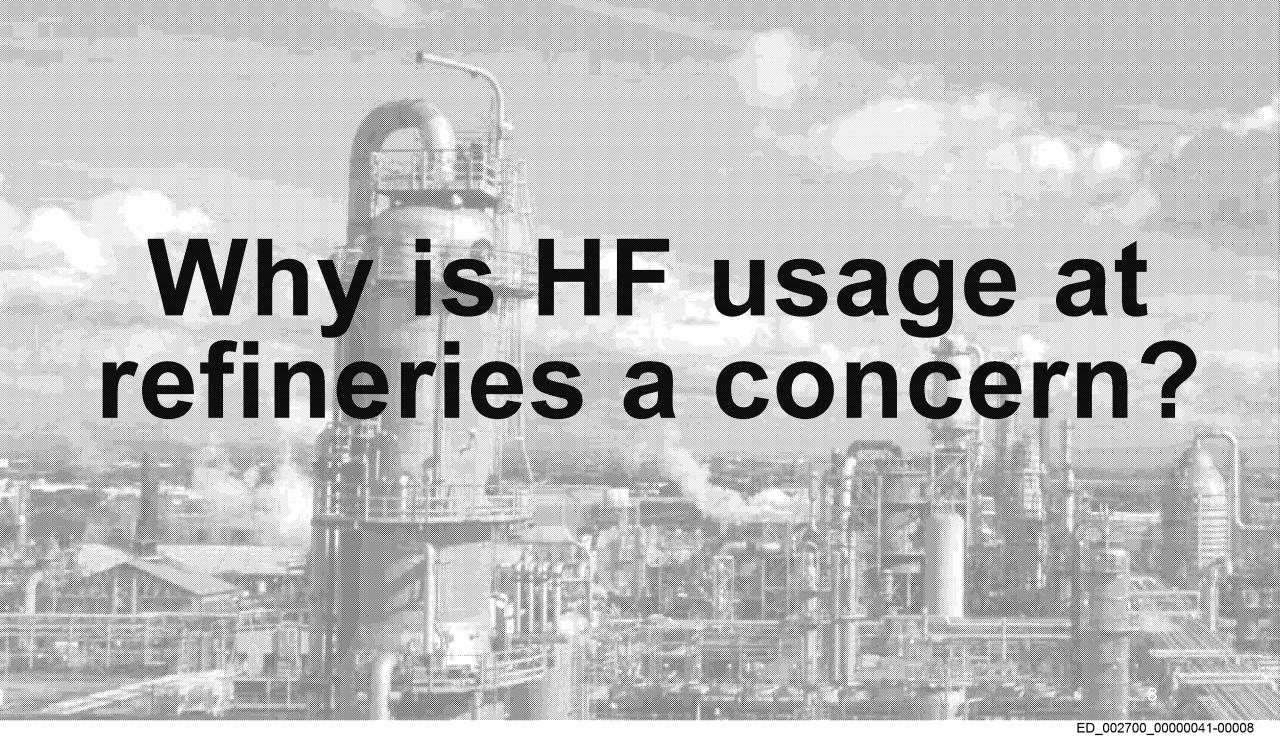
Refinery Committee Meetings

> Working Group Meetings

Individual Meetings 4 Refinery Committee Meetings

- ~ 600 attendees per meeting
- ~ 80 commenters per meeting
- 8 expert presentations

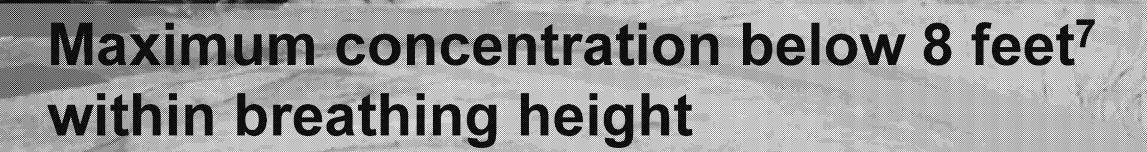
- 9 Rule Working Group Meetings
 - ~ 100 participants
 - 3 meetings in the community
 - 9 expert presentations



Refineries use large volumes of MHF...

2 inch hole could release 1,000 gallons in 2 minutes⁶

Ground hugging cloud upon release...

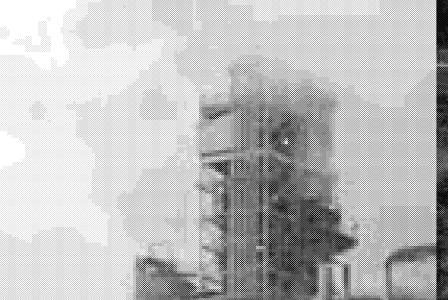


Based on Goldfish Study, Test 1 – Unmitigated release of HF

Rapid expansion of a vapor cloud upon release...

Tests have shown lethal concentrations can travel 2 miles⁸

Large-scale unexpected incidents such as...



System Failures



Natural Disasters Intentional Acts



Can lead to cascading failures



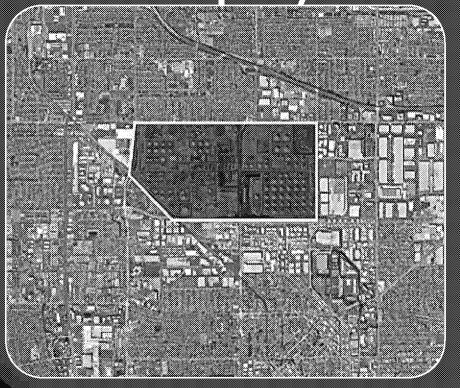
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High population densities...

Greater potential for widespread human harm

Torrance Refining

Company



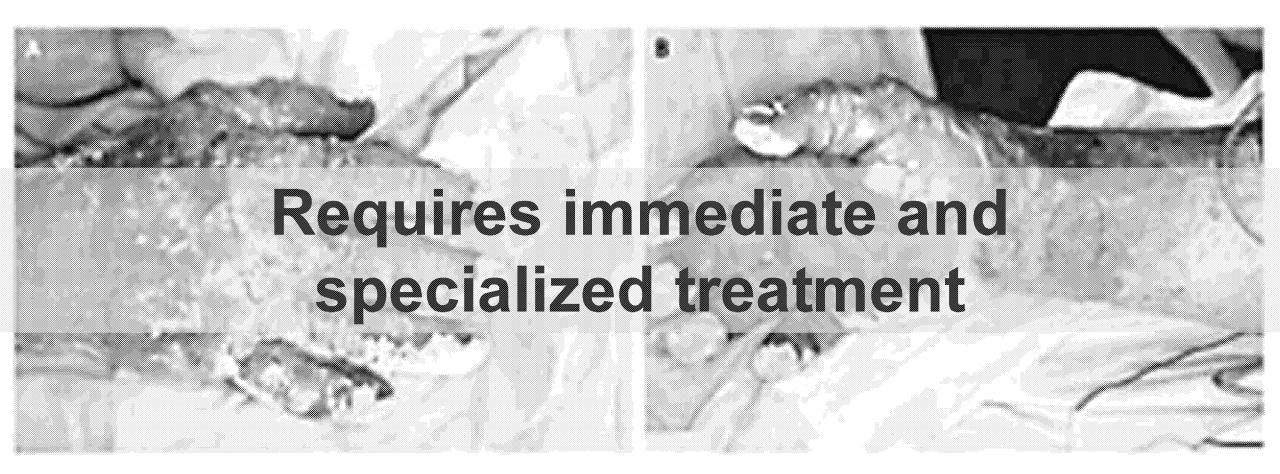
245,000 People within 3 Miles Nearest Residence ~0.3 miles

Valero Wilmington Refinery



153,000 People within 3 Miles Nearest Residence ~0.8 miles

Uniquely hazardous health effects that result in deep tissue and bone damage...



In 1986 Amoco and Allied **Signal Corporation** sponsored the "Goldfish" tests to assess HF release

Single release point was 1.65 inches (size of a golf ball)

1,000 gallons was released in 2 minutes

Ground hugging cloud travelled at wind speed of 18 feet per second

Cloud rapidly expanded upon release

HF concentration was twice the lethal level at 2 miles from release point

100% remained airborne



Field Tests

- Nevada Test Site
 - ☐ Goldfish test large scale outdoor testing
 - ☐ Hawk Test smaller wind tunnel tests on water spray mitigation



- Quest Consultants Inc. conducted two field tests for MHF⁹ (1992-1993) in Oklahoma
 - Mobil and Phillips
 - □ Texaco and UOP

HAZMAT apill Center	Nevada Test Site		
	Name	Year	Material
	Avocet	1978	LNG
	Burro	1980	LNG
	Coyote	1981	LNG
l two	Desert Tortoise	1983	Ammonia
	Eagle	1983	N_2O_4
	Goldfish	1986	HE

Hawk

1988

⁹ Both field tests were not at the current operating conditions (temperature, pressure, and additive concentration) used at refineries.

Acute Exposure Levels for HF for 10 Minutes¹⁰

Mild Health Effects

- 1 ppm
- Not disabling
- Notable discomfort
- Reversible health effects

Serious Health Effects

- 95 ppm
- Impaired ability to escape
- Long-lasting health effects
- Irreversible health effects

Lethal Health Effects

- 170 ppm
- Life threatening
- Death

HF Levels Measured in Goldfish Study

0.2 miles 27,000 ppm

0.6 miles 3,000 ppm

1.9 miles 400 ppm

Release Point

> 160 times the lethal level¹¹

18 times the lethal level¹¹ 2 times the lethal level¹¹

11 USEPA Acute Exposure Guideline Levels for 10 minutes exposure to HF

19

How much safer is MHF than HF?

Background on MHF

- Jointly developed by Mobil/Phillips in early 90's
- Modifier added to HF to reduce vapor-forming tendency
- Intent was for most of HF to rainout or fall to the ground
 - □ Initial additive concentration was ~30 percent, but led to "operational instability" 12
 - □ Additive concentration decreased to ~7 percent
- Torrance Refining claims that 50% of MHF will rainout

SCAQMD's Analysis of MHF

- Based on a review of technical documents and discussions with Torrance Refinery
 - □ Some, but uncertain, benefits of MHF
 - □ At most 35 percent benefit, but likely less
- No testing conducted at current operating conditions (additive concentration, pressure, and temperature)
- Most of the data is not publicly available
- Use of MHF is only one of many mitigation measures, but alone does not provide adequate safety for workers and community

HF and MHF Have Similar Concerns

- Ability of MHF to prevent formation of a vapor/aerosol cloud is highly uncertain
- Release of MHF will result in exposure to HF with same health effects
 - □ Any rainout will be HF liquid droplets
 - □HF vapor cloud will still form
 - □HF and MHF have same hazards and medical treatment

Material Safety Data Sheet

HYDROFLUORIC ACID, ANHYDROUS

I. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Hydrothoxic Acid, Ashydrous

OTHER/GENERIC NAMES: HF, Ashysison HF, AHF, Hydrogen Florride, HF Acid

PRODUCT USE: Chemical Derivatives, Alkelation Catalyst

MANUFACTURER: Homoywell International

Industrial Fluorines 101 Colombia Road

Box 1053

Morristown, New Jersey 07962-1053

Material Safety Data Sheet

MODIFIED HYDROFLUORIC ACID

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Modified Hydrofluoric Acid

OTHER/GENERIC NAMES: MHF, Modified HF, Modified Hydrogen Fluoride, Modified HF Acid Additized HF

PRODUCT USE: Alkylation Catalyst

MANUFACTURER: Honeywell International

Industrial Products 101 Columbia Road Box 1053

EMERGENCY OVERVIEW: Clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for all exposures.

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW: Clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for all exposures.

 Hydrofluoric Acid
 7684-39-3
 85

 Sulfolane
 126-33-0
 15

Trace impurities and additional material names not listed above may also appear in the Regulatory Information Section 15 towards the end of the MSDS. These materials may be listed for local "Right-To-Know" compliance and for other reasons.

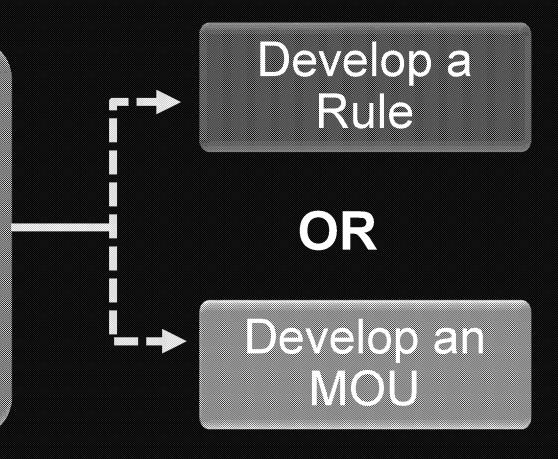
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Direction from Refinery Committee

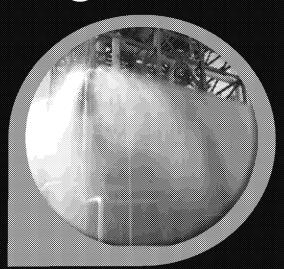
- Enhanced mitigation measures; and
- Phase-out MHF and explore option for a performance standard



Areas of General Agreement

HF and MHF are dangerous acids

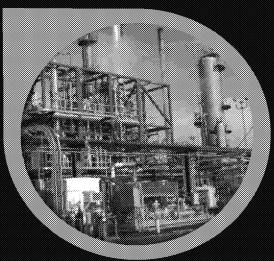




Enhanced mitigation measures are needed

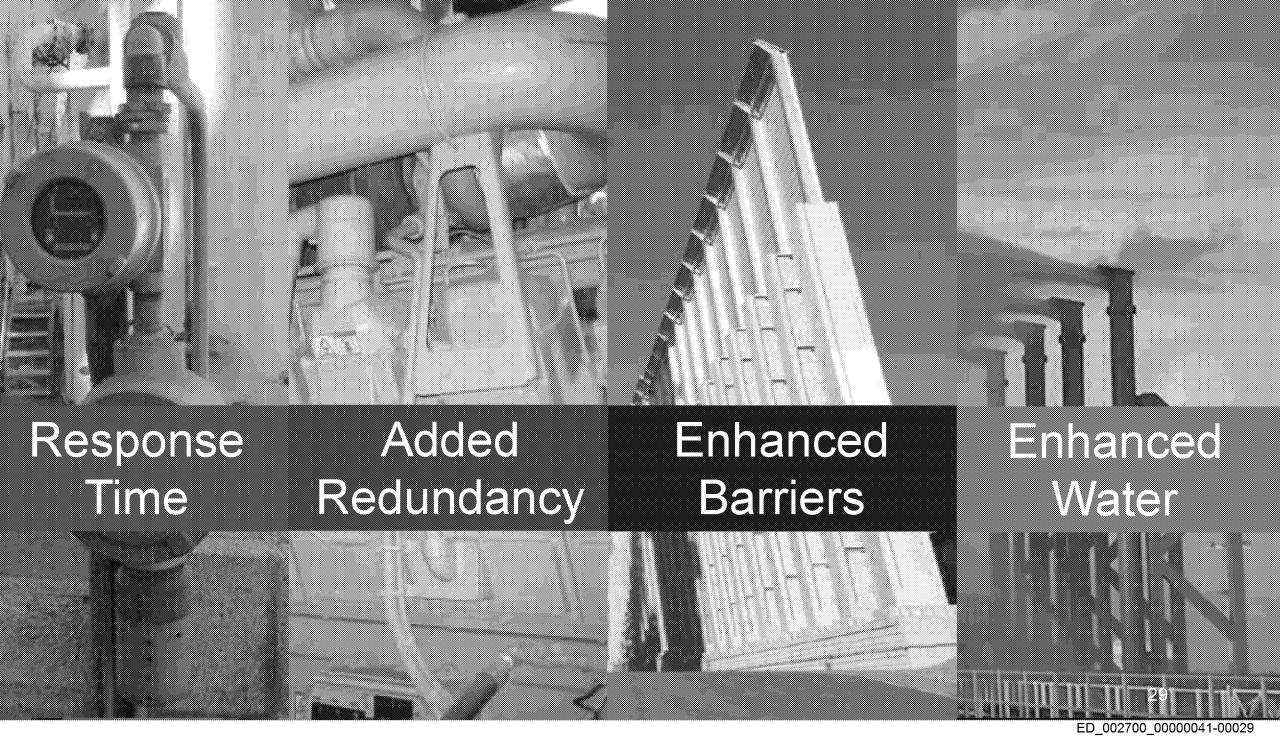
HF and MHF have the same health effects



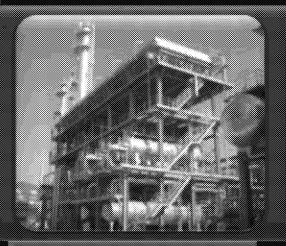


Other than sulfuric acid, additional time needed for other alternative technologies

Overview of Enhanced Mitigation

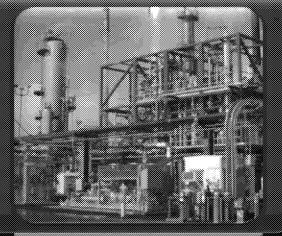


Alternative HF Technologies









Sulfuric Acid (Conventional)

- At 39 US refineries
- Safer than HF, but 50 more truck trips per day

Sulfuric Acid (Advanced)

- CDAlky uses 30-50% less acid – commercially proven
- ConvEx designed for HF conversion
 not commercially proven

Solid Acid Catalyst

- Petrochemical plant in China
- 2,700 bpd startup in 2015

lonic Liquid Catalyst

- Chevron, Salt Lake City
- Small pilot plant in 2005
- 5,000 bpd HF Alkylation conversion startup in 2020

Costs and Potential Market Impacts

- Torrance Refining's cost estimate of grassroots sulfuric acid unit¹³
 - \$600 million for alkylation unit
 - \$300 million for acid regeneration
- Valero has commented their facility has space constraints
- Advanced sulfuric acid units are expected to be substantially less
- Alternative technologies
 - Cost unknown
 - Torrance Refining views commercially viable as constructed at scale to California standards for two four-year turnaround cycles (Minimum of 12 years)
- Potential impacts to gasoline supply and cost
 - Any impacts would be temporary
 - Planned phase-out is different than an unplanned shutdown less disruptive

Discussion on MHF Phase-Out

No Phase-out

Yes Phase-out

Alternative technologies not commercially proven



Longer implementation schedule with a technology assessment

Phase-out could result in a gasoline shortage



Lead time to plan - other options for alkylate supply

Refineries state they have and will continue to use MHF safely



Uncertain a consequential release can be mitigated

Refinery estimate: \$900 million (Alkylation Unit and Acid Plant)



Lives at risk – cost of large release must be considered

Uncertain that Enhanced Mitigation Can Protect the Community

- Can consequential release be mitigated?
 - Can mitigation capture initial cloud?
 - Can water be deployed rapidly?
- Can the mitigation system target exact location?
- Can the refineries supply enough water?
- Can sufficient redundancy guard against system failure?



Performance Standard

- Benchmark that refineries would need to meet for continued use of MHF
- Needed to ensure enhanced mitigation can protect community
- Possible examples:
 - □ Concentration limit at fenceline or nearest receptor
 - □ Demonstrate MHF will not form dense vapor cloud
- 1991 Rule 1410 included a performance standard:
 - □20 ppm for 5 minutes; and
 - □ 120 ppm for 1 minute at the fenceline

Roši 1418 (Crail)

(Adapted April 5, 1990)

- STOCCESN FILTORIDE is adoptions, agreem or any organic median of implement fluoride.
- (b) LFFDACKLIN SLLDGBBB Schediff Pet PAINT is any peopling formsubsted to change ratio again particle in the hydropen Hazarda.
- (6) SEFERMENTE PROCEDENTS is one process in which hydrogen district is soot as a channel received to produce olderediscurvations, or hydrodistrationmentum.
- (80) MORREST, SEIDER MODERT CASE, APRODUSTALL SCHLAGE, a large encoderist of some occurring parties consistency specified as guidelines proposed by the Exercisive Officer. Each guidelines shall, is a mericansa, specify the following consistency.
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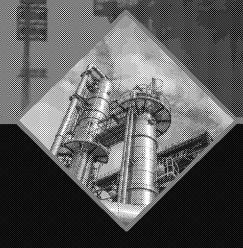
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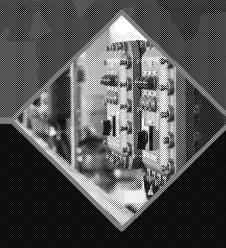
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Three Key Elements of Performance Standard







Release Scenario

- Key parameters
 - Rate of release
 - Locations
 - Unit parameters

Standard

- Performance standard that must be met if MHF is released
- Demonstrate standard is met through
 - Modeling
 - Testing

Staff is Seeking Direction

- Continue with approach based on direction from Refinery Committee
 - □ Develop rule or MOU that requires refineries to:
 - Phase-out MHF within 5 to 7 years; or
 - Demonstrate, based on enhanced mitigation measures, that they meet a performance standard (to be developed) that ensures a consequential release will not impact the community